IN-SITU REMEDIATION USING ELECTROKINETICS MIXING, INJECTION, AND TRANSPORT

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Introduction

SERDP Relevance

Thousands of DoD sites and installations are contaminated with organic pollutants and require clean-up. In situ remediation is an attractive and cost-effective option used to clean up contaminated soils. Key process additives for processes such as in situ oxidation and bioremediation are conventionally introduced by recirculating groundwater through the contaminated zone. However, complications of site geohydrology have restricted the transport and mixing of additives and resulted in inefficient field implementations. A technology for uniform introduction and mixing of additives has been a primary bottleneck to the successful field application of in situ remediation technologies. This project has demonstrated a new and innovative strategy for in situ cross-injection and mixing of amendments under single-phase and dual polarity pulse dc fields. In particular, the EK injection and mixing strategy has the potential to accelerate and stimulates in situ remediation of environmental contaminants in heterogeneous aquifers and leaky aquitards; both are major concerns for DoD, DOE, and EPA. This project supports and enhances current DoD research in the area of in situ restoration.

Summary

The ability to deliver amendments necessary for enhanced in-situ bioremediation to low permeability soils is the key to making in situ bioremediation a time and cost effective alternative to pump and treat systems for DNAPL remediation. Demonstrations of this technology that have relied on hydraulic delivery of amendments resulted in amendment delivery to predominantly high permeability areas in the subsurface. Site geohydrology restricted the transport and mixing of additives to the low permeability source zones and resulted in inefficient field implementations. With hydraulic amendment delivery, bioremediation occurs in the high permeability areas only, leaving the low permeability areas as source zones of contamination that continue to provide a contaminant mass for groundwater contamination. As a result, the time frame for in situ remediation with hydraulic amendment delivery is comparable to pump and treat timeframes. Effective amendment delivery is critical for successful and cost effective in situ bioremediation. This project demonstrates an effective, non-hydraulic delivery technique that based on the application of low level dc fields for accelerating and stimulating in situ remediation of low permeability, source-zone contaminants in at
sites contaminated with chlorinated solvents. Negatively charged amendments are injected under dc fields in soils by means of ionic migration. Ionic migration is the process by which ions migrate in solution to the electrode opposite in polarity. This transport process is dependent on the strength of the electric field, and ionic mobility of the specific ion. The study evaluated the transport of three potential amendments (citrate, lactate and permanganate) at two concentrations (1000 mg/l and 10,000 mg/l) in three soil configurations (homogenous sand, homogeneous clay, layered clay in sand) under two different electrode spacing (40 cm and 100 cm) with the application of two current levels (2 and 5.3 A/m2). Control tests were also conducted to compare the transport rates to those under hydraulic injection. The transport of a non-reactive tracer (bromide) under electric and hydraulic fields was also evaluated to access the amendment degradation rate relative to transport rates.

This study demonstrated that:
Citrate and lactate delivery rate under 1 V/cm corresponds to an equivalent hydraulic gradient of 150 to 215 in a homogeneous soil system for hydraulic delivery in a similar soil system. For the 40 cm EK, cells this would be and equivalent hydraulic head for the citrate and lactate delivery of 60 and 85 meters respectively.
-Electokinetically delivered amendments follow the electrical field lines and move through low permeability areas in heterogeneous systems. This eliminates the short-circuiting of amendments through high permeability soil areas that is predictably observed under hydraulic amendment delivery.
-Biological fouling at the injection points does not significantly reduce the rate of amendment introduction over time as observed in hydraulically delivered amendment systems. Increases in biological activity were observed in the low permeability soils during electrokinetic amendment delivery. The electrical field was not observed to negatively affect the biological system in the soil.

The study clearly demonstrated the potential of injecting negatively charged amendments to stimulate bioremediation.

**Objective**

The purpose of this one-year study was to demonstrate that electrokinetic transport of amendments in low permeable homogeneous and heterogeneous soils for in-situ bioremediation is feasible and superior to hydraulic delivery methods currently used. This study evaluated the rates of cross injection and mixing of additives (lactate, citrate and permanganate) in soil (sand and clay) by ionic migration and electroosmosis under single-phase and dual polarity pulse dc fields. The study also evaluated the impacts of soil heterogeneity on the uniformity of transport.

**Background**

**Bioremediation**

In situ bioremediation is an attractive and often cost-effective option to clean up contaminated soils. The process utilizes microbial activity in the soil to degrade or
transform organic contaminants into non-toxic produces. Microbial processes require an electron donor, macronutrients (e.g., nitrogen and phosphates), micronutrients, trace nutrients, and an electron acceptor. In microbially-mediated cometabolite transformations, an additional external electron donor is required. In some cases, inducers may be needed to trigger the microbial transformation reaction.

Generally, the initial transformations of highly chlorinated CAHs, such as PCE, CT, and 1,1,1-TCA, are more effective under reducing conditions due to their relatively high oxidation state. Reductive dechlorination of such compounds can occur under iron-, nitrate- and sulfate-reducing and methanogenic conditions (Freedman and Gossett, 1989; Bagley and Gossett, 1990; Bouwer, 1994). Reduction rates are greatest in highly chlorinated compounds (such as tetrachloroethylene and carbon tetrachloride) and tend to decrease in the less chlorinated daughter compounds (such as vinyl chloride and chloroform) (Cookson, 1995). Oxidation of chlorinated hydrocarbons, as a sole carbon source or via cometabolism, is also possible under aerobic conditions (Hartman et al., 1985; Little et al., 1988; Tsien et al. 1989; Ensign et al., 1992; Hopkins et al., 1993). In contrast to anaerobic reductive dechlorination, the rate of oxidation under aerobic conditions decreases with increasing chlorination of hydrocarbons. Two-phase, sequential anaerobic/aerobic systems have been proposed by researchers to achieve complete transformation of CAHs (Cookson, 1995).

Recently, studies showed that hydrogen could serve as a key electron donor. Fennell et al. (1997) evaluated the performance of butyric acid, propionic acid, (low H2 producing donor), ethanol, and lactic acid, (high H2 producing donor) as hydrogen donors for PCE dechlorination in short-term and long-term serum bottles experiments. While shorter-term experiments showed some variations, the longer-term experiments, resulted in significant dechlorination rates. Ballapragada et al. (1997) showed that dechlorination rate was rapid in cultures fed with H2, lactate, or propionate, but the rate was very slow in unfed cultures or acetate fed culture. Carr and Hughes (1998) showed that lactate, methanol and H2 addition produced similar effects on PCE dechlorination. Enrichment with methanol, lactic acids, or H2 caused significant dechlorination rates after 20 days. Methanogenesis and dechlorination occurred simultaneously and neither inhibited the other. Song et al. (2002) summarized the results of a field demo of sodium lactate pulse injection for stimulating bioremediation of in situ reductive dechlorination of TCE contaminated site at Idaho National Engineering and Environmental Laboratory’s (INEEL). The results demonstrated that lactate injection stimulates dechlorination of TCE to ethene as electron donor. However, the results indicated that lactate did not enhance dechlorination of t-DCE. In a pilot-scale test, Major et al. (2002) showed that injection of methanol and acetate did not impact dechlorination, as VC and ethene were not detected after more than 100 days. After that, KB-1 was injected and Dehalococcoides (the special organism group which correlated with complete dechlorination of CE to ethene), VC, and ethene were detected at the site. Ethene was the dominant compound within the site after 318 days.

Efficient injection of organic acids, such as lactate and citrate, in heterogeneous deposits is key factors for successful in situ degradation of chlorinated solvents. Injection methods are generally based on hydraulic flow systems. Such systems are most effective in high permeability (e.g., greater than $10^{-3}$ cm/s) soils such as sandy aquifers and few have been developed to address soils with lower permeability.
Additive delivery is generally the limiting factor for in-situ dechlorination of heterogeneous deposits. Yang, and McCarty (2000) demonstrated the bioremediation of high concentrations of contaminants, DNAPLs, near the solubility limit is possible, and long as a high enough concentration electron donor is present.

Ebihara, Tatsuji, and Bishop, Paul L (2002) demonstrated that the addition of acetate increased the biomass of PAH-reducing microbial populations. He, et al. (2002), concluded that at some contaminant sites, acetate and not H₂ is the relevant direct electron donor for PCE to cis-DCE dechlorination, and that acetate alone is sufficient to sustain complete dechlorination to ethane biphenyls.

Transport and Electrokinetics

DC electric fields provide efficient injection and mixing strategies of remediation additives. Studies show that electric fields can move ions into low permeability soils (<10⁻⁷ cm/s) at efficient and uniform rates. It is reported that transport rates of several centimeters per day have been observed (Acar and Alshawabkeh 1993; Acar et al. 1996; 1997; Gent et al. 2001).

This study evaluates the reactive transport rate of selected organic acid anions in low permeability clay soil by ionic migration. Organic acid anions will undergo sorption and degradation in the soil, which will retard its transport. Furthermore, electroosmosis can oppose ionic migration of anions and can further retard its transport rate. Ultimately, the dc fields will serve as a delivery method to enhance bioremediation, and will not replace biological transformation.

Transport mechanisms under electric fields (Figure 1) are electroosmotic advection (or electroosmosis), electromigration or ion migration, and electrophoresis (Mitchell 1993). Electroosmosis mobilizes the pore fluid in the soil; usually the flow direction is from the anode toward the cathode, while electromigration effectively separates the anions (negative ions) and cations (positive ions) via transport to the anode and cathode, respectively (Alshawabkeh and Acar, 1992). Electrophoresis describes the transport of charged particles, such as clay particles or bacteria, under the applied electric field to the electrode opposite in polarity. In this project, electroosmosis and electromigration are the target mechanisms for delivery of additives into heterogeneous aquifers and leaky aquitards. Transport rates under these processes can be calculated by,

\[ J_i = c_i u_i i_e + c_i k_e i_e \]  

where \( J_i \) (MT⁻¹L⁻²) is the flux of species or ion i due to ion migration and electroosmosis, \( c_i \) (ML⁻³) is the concentration of i, \( u_i \) (L²T⁻¹V⁻¹) is the effective ionic mobility of i, \( k_e \) (L²T⁻¹V⁻¹) is the coefficient of electroosmotic permeability and \( i_e \) (V L⁻¹) is the electric gradient.

The rate of electroosmotic flow is controlled by \( k_e \), which is a measure of the rate of fluid flow per unit area under a unit dc gradient. The value of \( k_e \) is widely accepted as a function of zeta potential of the soil particle surface, viscosity of the pore fluid, porosity, and electrical permittivity of the medium. The value of zeta potential is dependent upon pore fluid’s ionic strength and pH. The impact of electrochemical changes (e.g., pH and ionic strength) during application of electric currents on zeta potential and electroosmotic permeability has been demonstrated (Hunter, 1981; Eykholt and Daniel, 1994; Eykholt, 1997; Vane and Zang, 1997). As an example, un-
amended single polarity electroosmosis has the effect of creating strong pH-Eh gradients. This in turn can affect the electrode material, gas evolution that can interfere with current flow, the pore chemistry, the zeta potential, and possibly cause heavy metals precipitation in some cases. A careful measurement of pH dependence of the zeta potential in Kaolinite clay (Lorenz, 1969) shows that a zero isoelectric point the pH approaches a value of 4.0. This would have a detrimental effect on any electroosmotic transport. Therefore, proper control of electrolyte strength and pH at the electrodes, and consequently the treatment area, is necessary for efficient electroosmotic flow.

Electric fields have been used for electroosmotic extraction of organic contaminants from soils (Shapiro et al., 1989; Acar et al., 1992; Bruell et al., 1992). Recently, Monsanto led a team to evaluate the use of electric fields for electroosmotic extraction of TCE from a site in Paducah, Kentucky, using layered horizontal electrodes, or the “Lasagna™” process (Ho et al., 1997; 1999a; 1999b). The mechanisms of interest in this proposal are different from those used in electroosmotic extraction (e.g., the Lasagna™ Process). This study investigated strategies to stimulate remediation by electrochemical methods, while the Lasagna™ process mainly uses electroosmosis for extraction of TCE from the soil into electrode treatment zones. The time estimated for 99% electroosmotic extraction of benzene, TCE, toluene, m-Xylene, and hexane are still on the order of several years (depending upon electrode spacing), and may take longer in aquitards. Isooctane is predicted to require 17 years of electroosmotic extraction to achieve 99% removal. The general tendency is for substances with high water solubility and low distribution coefficients to require less energy and time for transport, while those with low water solubility and high distribution coefficients to take longer for
transport. While the Lasagna™ process has shown success in recent tests, one major advantage this technique is that it can degrade trapped, immobile and adsorbed contaminants that cannot be extracted via electroosmotic flow.

Application of electric currents will also result in electrolysis reactions at the electrodes. If inert electrodes (such as graphite or ceramic-coated electrodes) are used, then water oxidation produces oxygen gas and acid (H$_3$O$^+$) at the anode (positive electrode) while water reduction produces hydrogen gas and base (OH$^-$) at the cathode (negative electrode), as shown in equations 2 and 3,

\[
\begin{align*}
2\text{H}_2\text{O} & \quad \Rightarrow \quad 4\text{e}^- \quad + \quad 4\text{H}^+ \quad + \quad \text{O}_2 \quad \text{Anode} \quad (2) \\
2\text{H}_2\text{O} \quad + \quad 2\text{e}^- & \quad \Rightarrow \quad 2\text{OH}^- \quad + \quad \text{H}_2 \quad \text{Cathode} \quad (3)
\end{align*}
\]

Faraday’s law for equivalence of mass and charge can be used to calculate the rate of redox reactions will occur at the electrodes (Koryta and Dvorak, 1987). There is the distinct possibility that electrodes could be engineered not only to accelerate amendment transport, but they may also be utilized to produce the desired amendment.

Electric fields may also produce an increase in soil temperature. Temperature increase due to current application will depend upon the field strength and resistivity of the medium. Acar and Alshawabkeh (1996) reported 10°C increase in temperature in a large-scale test conducted for the extraction of lead from kaolinite in which no additives were used to control electrolyte pH. In soils with elevated temperatures, mesophiles predominate at temperatures between 20 and 45 °C (Gaudy and Gaudy, 1988). At temperatures above 45 °C, the dominant microbial community will be thermophiles. EK systems could be engineered to modify soil temperatures for enhancing both transport and bioremediation in winter conditions or cold climates. The effect of temperature increases on microbial community structure changes, transport of contaminants and nutrients, and subsequent bioremediation should be considered in an integrated EK approach.

Finally, abiotic inorganic oxidants such as potassium permanganate or hydrogen peroxide have been known to degrade organic environmental contaminants. EK is expected to have an improving effecting on the management and minimization of such additives in soils and this should improve the overall effectiveness of in-situ remediation process.

**Dual Polarity Pulse dc Fields**

Single-phase dc fields produce extreme pH and $E_H$ conditions at the electrode and amendments or enhancements may be needed to optimize the system. Another approach is to use an asymmetric, reversing polarity field as shown in Figure 2. For simplicity, this scheme is commonly referred to as Electro-Osmotic Pulse, or EOP. The dual polarity pulse (Figure 2a) characteristics can be described by the five parameters: $V_a$ = magnitude of applied positive potential; $V_b$ = magnitude of applied negative (reversed) potential; $t_A$ = duration of applied positive potential; $t_B$ = duration of applied negative (reversed) potential; $t_C$ = duration of “rest time” with no potential applied. This EOP approach is currently being applied commercially to de-water concrete at the U.S. Treasury Building in Washington, DC, and similarly in buildings at Ft. Monmouth, Ft. Jackson, Ft. Sill, Aberdeen Proving Grounds, and at various facilities managed by the Tank Automotive Command. The primary U.S. patent granted for use in concrete is US
5,368,709, “Method and Apparatus for Controlling the Relative Humidity in Concrete and Masonry Structures” (Kjell Utklev, filed 4/12/94). In addition to the success of using an EOP approach at sites with poured concrete basements, recent work has found that polarity reversal without a rest period improved effectiveness, reduced consumption, and neutralized the adverse effects of electrolysis during dewatering of mine tailings (Shang and Lo, 1997). The dominant theory for the mechanism of migration enhancement is based on reducing the tortuosity limitations to migration in pore fluids. Figure 2a shows the three main phases of a single characteristic positive and negative dc pulse that is repeatedly cycled. The initial time positive pulse (A) is the longest in duration and causes migration of cations and water molecules toward the cathode until an obstruction is encountered. The negative pulse (B) is much shorter and causes any blocked cations and water molecules to back up a short distance from an obstruction. The last period (C) involves a period of time with the absence of applied electrical current. During this time the pore fluid containing additives will randomly migrate to become displaced from their original obstructed path and are able to progress forward when the pulse is repeated. Tortuosity limitations in soils may likewise be similarly reduced.

Figure 2: (a) Characteristic EOP with Defining Parameters (b) Possible predominant transport directions depending on time sequencing of electrode polarities. Circular example shown would result from a time dependent vector superposition or addition.

By expanding on this technology, enhanced subsurface mixing could be achieved. Figure 2b shows a single set of two segment anodes inserted into the ground. As shown, the anode segments are labeled A through D. Water migration between any two electrodes could be achieved through application of an optimized electroosmotic pulse. For example, using electrodes A and C (or B and D) surface water seeded with chemical/biological additives could be used to enhance vertical transport. Alternatively, by using a time sequence of an applied EOP between various electrodes, a net additive superposition of a circular mixing action could result. Two rows of corresponding electrode pairs could be used for mixing in pits. Figure 3 shows an example of a circular configuration. By applying an optimized EOP from the top electrode to the corresponding opposite bottom electrode, and additionally switching
between electrode pairs in a circular fashion, a kind of downward spiral or auguring migration of surface water could be induced. In addition, the more cost effective mixed-metal oxide electrode materials can be optimized for remediation. In the later phases of this study, various lessons and experiences based on cathodic protection technology will be adapted and applied in the design and implementation pilot investigation.

Figure 3: Circular electrode configuration showing result of sequential phasing of predominant downward migration directions between electrode pairs

Findings Summary

The findings from the 40 cm electrokinetic delivery studies provide the rates of amendment delivery in low and high conductivity soil systems. The rates of amendment migration allow the comparison of the effectiveness of EK amendment delivery in homogeneous systems to the delivery rates obtainable using hydraulic amendment delivery.

Figure 4 displays graphically the effective hydraulic gradient that would be required to move amendments through both sand and clay soils at a rate that is equal to that observed for the electrokinetic delivery of the organic amendments lactate and citrate. Citrate and lactate delivery under achievable field scale electrochemical conditions is 150 to 215 times more rapid in low permeability soils than hydraulic delivery. In order to achieve the delivery rates observed under electrokinetic conditions, a hydraulic gradient in a homogeneous soil system of 150 for citrate and 215 for lactate would have to be applied. The delivery of amendments to low permeability soils is a problem using existing technologies. It is not surprising that advantages in the rate of electrokinetic delivery over hydraulic delivery are observed. The movements of amendments through low permeability soils that make up the confining lenses and source zones for DNAPL contamination in the subsurface is the challenge that limits the effectiveness of current in situ remedial systems using enhance bioremediation. The significant advantage provided through the application of dc electrical field through such soils for the delivery of lactate and citrate amendments is an indication of the potential application of this technology for cost and time effective enhanced biological remediation.
The increased rates of amendment delivery in homogeneous systems identify the advantageous of electrochemical amendment delivery, but the subsurface hydrology in DNAPL source zones cannot be considered homogeneous systems. Areas of low and high permeability exist and control the hydraulic flow of amendments and contaminants. To say that electrokinetic delivery of citrate is equivalent to the application of a hydraulic gradient of 150 implies that the application of such a head is possible. The hydraulic system will preferentially move the amendments around areas of low permeability due to the non-uniform nature of hydraulic flow in these systems. The electrokinetic delivery of charged amendments is governed by the electrical field lines established through the soil systems by the electrode materials, the voltage applied, conductivity in the subsurface, and electrode geometries.

As a result, the electokinetically delivered amendments will not avoid areas of low permeability but follow the electrical field lines and produce a more uniform flow in heterogeneous soils. This can be shown in the results from the movement of lactate and citrate in 40 cm cells that were prepared with both low conductivity clay layers and high conductivity sand layers as shown in Figure 5. Samples taken from the interior of the clay layer in these systems shows that the movement of the amendment is governed by the electrical field established between the electrodes. An increase in concentration of the amendment and the biological transformation products of the amendments were observed within the low permeability areas in these soils. The demonstration of this fundamental electrochemical principle in heterogeneous soil systems defined a second, significant advantage of electrokinetic delivery of amendments over the hydraulic delivery. That is the ability to direct the movement of
the amendment to the low permeability source zones of DNAPL contamination in the heterogeneous subsurface soil systems.

Another finding of the preliminary effort investigating the effectiveness of electrokinetic delivery of amendments for enhanced in situ bioremediation is the effect of electrode distance on the rate of delivery of charged amendments. The electrode-to-electrode distance is an important factor in the installation costs associated with the field demonstration of this technology. There are some similarities between the placement of electrode wells for electrokinetic delivery and placement of amendment addition wells for hydraulic amendment delivery. Both are a cost factor for technology implementation with an inverse relationship between the spacing and the effectiveness of treatment with regards to treatment time and full coverage of the contaminated zone. A series of experiments were performed during the initial year of the development of electrokinetic amendment delivery systems with a range of electrode distances.

These experiments were performed under electrokinetic conditions that are realistic for field application with electrode-electrode distances of 40, 100, and 200 cm. The transport rate of anionic amendments observed was similar for all three distances (12 cm/day to 27 cm/day in sand). Over the range of distances, studied, systematic decreases in the delivery rate were not observed at increase electrode spacing. A field application at Point Mugu California involved the introduction of citrate at the cathode well. Citrate concentrations were monitored in the anode well during the course of the study. At this site, the cathode-anode distance is set at 4.6 m (15 ft). This field scale application was effective at transporting citrate to the anode compartment in 15 days. The upper limit for electrode distances that will allow the delivery of amendments has not been established. The distance at which the rate of amendment delivery will
decrease to rates below those feasible for field use is dependent on a number of factors including soil conductivity, the rate of biological transformation of the amendment, amendment reactivity with the soil and electric field strength. The continued research effort will evaluate the upper limit of electrode spacing based on specific site biogeochemistry. Nothing in the present effort indicates that electrode-electrode distances will not be comparable to the injection well placements that have been used for hydraulic delivery of biological amendments or chemical oxidation compounds during site demonstrations of hydraulic delivery.

There are a number of important findings from the first years work on EK delivery regarding the biological responses to electrochemical delivered amendments. One of the significant drawbacks for field demonstration of enhanced in situ bioremediation is biological fouling of the injection wells. Large amounts of biomass forming in and near the well points that amendments are introduced from effectively reduce the hydraulic conductivity and decreases the amount of amendment that can be introduced over the lifetime of the well. In some cases, this fouling happens rapidly enough that new injection wells are regularly required leading to increased costs for the remediation. In lactate and citrate electrokinetic delivery experiments performed with sand and clay, some biological growth was noted in the electrode compartments and in the soil system adjacent to the electrode wells. This growth however, did not significantly alter the rate at which the amendments were delivered. It appears that the migration of the anionic amendments was not significantly retarded even as the biomass reduced the hydraulic conductivity in the soil near the electrode. This finding was verified at Point Mugu. After one-year of continuous operation with citrate addition, no biomass fouling has been observed. This is thought to be a result of the conducting nature of the biomass and the lack of the necessity for bulk water motion to transport ions. No significant effects on the soil microbiological systems were observed. Increased microbial populations in the soil during the EK amendment delivery were verified by enumeration of the aerobic heterotrophs using PCA agar.

The research performed over the last year strongly suggests that current in situ enhanced bioremediation technology could be made significantly more effective if electrokinetic delivery of biological amendments was used instead of hydraulic delivery. The greatest benefit would be the ability to stimulate biological activity in low permeability clay areas of the subsurface that act as DNAPL source zones. The technology has been demonstrated to increase delivery rates by over two orders of magnitude faster than under a unit hydraulic gradient, deliver soils to low permeability areas in heterogeneous soil systems, and allow amendment delivery over distances which lend themselves to field applications. The research required to take this technology to the point where a field demonstration of a DNAPL source zone remediation as outlined in the original SERDP proposal and includes the necessary microbiological and contaminant fate research that will be required along with continued electrokinetic system design research. The development of this technology is expect to resulting great cost savings to DoD, DOE and EPA stake holders along with industry and other landowners where DNAPL contamination exists that has the potential to affect groundwater.
Experimental

Experimental setups, baseline testing, and controls were standardized for all single direction transport tests conducted by different institutions. The same soil types, initial pH conditions, electric energy, and electrode spacing were used. The two soils used throughout this study are fine sand and clay. The sand is OK-110 from US Silica and the clay, named Gessie, is from Miami County, Indiana. The soils were collected at the beginning of the study homogenized and characterized. Steps were taken to insure that enough soil is prepared so that a single homogenized soil (for each soil) can be used throughout this first year’s investigation. These soils were selected to reflect magnitude variations in hydraulic conductivities, ranging from $10^{-3}$ cm/sec for sand and $10^{-7}$ cm/sec for the clay. The experiments were developed to evaluate transport under homogeneous and heterogeneous (stratified) conditions. The three additives were used for this investigation include two organic acid anions (lactate and citrate) and one inorganic anion (potassium permanganate).

The experiments were organized under several task including EK experiment cell design, preliminary testing, homogeneous soil experiments (40 cm cells), heterogeneous soil experiments (40 cm cells, large spacing (1 and 2 meter cells, Electro osmotic pulse (40 cm cells), and modeling.

Materials and Analytical Methods

Soil Preparation and Characterization

The Gessie clay was manually collected and prepared as follows. The first foot of soil on the ground was eliminated, due to the amount of roots, debris, and heterogeneities present in this horizon. The collected soil was air dried in large flat pans and was frequently turned and mixed to facilitate drying and homogeneity. After drying the soil was processed through a hammer mill to remove large soil chunks and create homogeneous soil particles. The soil was analyzed for physical and chemical properties. X-ray diffraction analysis showed that the sandy clay soil contained minor amounts of dolomite and the US Silica sand was almost pure quartz, Dolomite is a hydroxy-interlayered smectite.

The compaction properties were obtained from a modified version of the standard proctor test using 15 blows per each of 3 layers with a 2.5-kg (5.5lb) hammer and a 30.48-cm (12-inch) drop on a 10.2 cm (4 inches) diameter mold (ASTM D-698). The soil properties are described in [Table 1](#).
Table 1: Clay soil chemical and geotechnical properties

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<td>Median Pore Diam. (m*10⁻⁶)</td>
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<td>Total SO₄²⁻ (mg/kg)</td>
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<td>PH of 20% Slurry</td>
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<td>Total Cl (mg/kg)</td>
<td>&lt;31</td>
<td>Maximum Pore Diam. (m*10⁻⁶)</td>
<td>0.257</td>
<td>Maximum Pore Diam. (m*10⁻⁶)</td>
<td>0.257</td>
</tr>
<tr>
<td>BaCl₂ Ext Fe (mg/kg)</td>
<td>3.1</td>
<td>CEC (meq/100g)</td>
<td>15.3</td>
<td>CEC (meq/100g)</td>
<td>15.3</td>
</tr>
<tr>
<td>BaCl₂ Ext Cl (mg/kg)</td>
<td>0</td>
<td>TKN (mg/kg)</td>
<td>1090</td>
<td>TKN (mg/kg)</td>
<td>1090</td>
</tr>
<tr>
<td>BaCl₂ Ext Mg (mg/kg)</td>
<td>131</td>
<td>NH₃ (mg/kg)</td>
<td>6.83</td>
<td>NH₃ (mg/kg)</td>
<td>6.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NO₂/NO₃ (mg/kg)</td>
<td>12.1</td>
<td>NO₂/NO₃ (mg/kg)</td>
<td>12.1</td>
</tr>
<tr>
<td>Total P (mg/kg)</td>
<td>655</td>
<td>PO₄³⁻ (mg/kg)</td>
<td>2.34</td>
<td>PO₄³⁻ (mg/kg)</td>
<td>2.34</td>
</tr>
<tr>
<td>TOC (mg/kg)</td>
<td>14296</td>
<td>Zeta Potential (mV)</td>
<td>-75.2</td>
<td>Zeta Potential (mV)</td>
<td>-75.2</td>
</tr>
</tbody>
</table>

Experimental Setup
A uniform cell design is utilized by all labs conducting EK studies. The experimental cells are made of acrylic and consist of a rectangular box having a 5-cm height a 5-cm width and a 40-cm length as shown in Figure 6. Acrylic reservoirs at the end of the cell are designed to hold the electrodes and prevent them from contacting the soil specimen directly, thus allowing electrolyte cycling and amendment addition. In addition, liquid tanks having a volume of 500 mL to 1000 mL are available for each electrode reservoir. These tanks provide the ability to add make up liquid to the cell tanks. These tanks also facilitate the addition of amendments and permit pH measurements without any electrical interference. Electrodes, made of either a sacrificial (reactive) or non-sacrificial (inert) material, were used as part of this study and were placed in the reservoirs. Zero head difference was insured across the cell to minimize the influence of non-electroosmotic water movement. pH-control pumps were used to circulate the electrolytes and provide the required chemistry in the reservoirs. Catholyte and anolyte pH and electric conductivity were monitored throughout the duration of the experiment. Voltage, current, and flow measurements were conducted daily.
The preparation of the cells was performed in a manner by which the soil compaction was similar to that expected to be found in subsurface soil systems (ASTM D-698) Tests were conducted using homogeneous samples. The effect of heterogeneity was evaluated by preparing a three-layer soil sample in 2D configuration as displayed in Figure 4. A clay layer (5 cm depth and 20 cm length) was placed (compacting 15 blows per 1000 cm$^3$ of soil placed in the cell) and surrounded by sand. Sampling ports were placed at equal spacing between the anode and cathode at three levels. The ports were numbered 1 to 4 from anode to cathode and were used for pore fluid sampling, voltage and pH measurements whenever possible. Additives tested include two organic acids (lactic acid and citric acid) and one inorganic additive (potassium permanganate). Additives were injected at the cathode (in some experiments additives were also added at the anode). Experimental setups, baseline testing, and controls were standardized for all homogeneous and heterogeneous transport tests conducted by different institutions. The same soil types, initial pH conditions, electric energy, and electrode spacing were used. Figure 7 illustrated the recirculation system and pH control used in these experiments.

Samples were collected during and after testing for analysis. Organic acid anion analysis was conducted by ion chromatography using either a Dionex DX-100 or a DX-500 with and Dionex AS11 column as outlined in U.S. EPA Method 300.1. Potassium Permanganate analysis was by Standard Methods for the Examination of Water and Wastewater 4500-KmnO$_4$. Voltage and current readings were taken directly from power supplies and by using a portable multimeter. pH and ORP readings were taken by various pH electrodes and pH meters.
Results and Discussion

Screening Tests
An initial series of experiments was conducted under single-phased dc fields to narrow the number of parameters. These tests consisted of a series of relatively short experiments (few hours to few days) to select the best operating parameters for the specified soils and additives. These operating parameters are current or voltage controlled power, the optimal power setting (low or high) utilized throughout the study, if sacrificial or non-sacrificial electrode should be used, and if the effects of concentration of the amendments need to be considered throughout the remainder of the experiment. Citric acid and sodium citrate was selected as a representative amendment during the initial screening tests. Eight experiments were conducted to determine the effects of power operating mode (amperage versus voltage control). Eight additional experiments were conducted after the power operating mode testing is completed to determine the effects of sacrificial and inert electrodes on the efficiency. Additional eight experiments were conducted to determine the effects of amendment concentration on the transport
rate. Twenty-four initial screening experiments were conducted. The results provided preliminary evaluation of best testing conditions/parameters for conducting the transport studies. Based on the results, the following testing parameters were selected: Two soil types (high and low permeability), two power settings at constant current density (0.5A/m² and 2 A/m²), inert electrodes only (graphite), and low/high additive concentrations of 1,000 mg/l and 10,000 mg/l). Electrolyte pH should be maintained around 4-5 at the anode and around 8 at the cathode.

Inert electrodes were chosen for these experiments because they resist plating creating a more efficient system. Precipitants do not form in the electrode chamber as long as the pH is maintained close to neutral. It is important for the pH to remain neutral to promote biological activity and to prevent precipitation in the cathode chamber. The amendments were chosen carefully for those reasons. Citric acid was used to maintain the pH on the cathode side for the citrate experiments and lactic acid was used for the lactate experiments. When additional concentrations of citrate and lactate were needed, they were added in the form of sodium citrate and sodium lactate.

Distilled water was used in initial experiments. However, distilled water increased the time needed equilibrate or ionize the system at the desired current density so tap water was employed for all experiments. Tap water or potable water became the water of choice after discussions among the team members. Tap water was chosen because it is already ionized, shorted the equilibration time at startup, and readily available in the large volumes needed. Since ions in tap water are in low concentrations, they had minimal effect on the transport of the amendment. This is because the amendment concentration at the cathode was maintained at a target concentration of 10,000 ppm. The transference number for a given ion, $t_j$, is the contribution of that species made by that species divided by the total conductivity of all species in the bulk solution. The equation for the transference number of a given ion is:

$$ t_j = \frac{i_j}{i} = \frac{|z_j|u_jC_j}{\sum_k |z_k|u_kC_k} $$

where $z_i$ is charge number of the ion, $u_i$ is the ion mobility, and $C_i$ is the concentration of the individual species. The concentration from the amendment overwhelms all other ions in the solution.

**Detailed one dimensional 40 cm experiments**

With the power operating mode, electrode type, and amendment concentration established, a second series of detailed experiments was conducted using the fine sand and clay soil to determine the effects of different soils and amendments on the rates of transport. The amendments used were lactic acid, citric acid, and potassium permanganate. To insure a direct comparison with EK, hydraulic advection tests were conducted using only a differential hydraulic head to facilitate amendment transport. A non-reactive tracer EK experiment using bromide was conducted to demonstrate the effectiveness of ion migration without the biological degradation associated with using organic acid ions. Experimental parameters for the experiments are summarized in Table 2.
Table 2: Detailed 40-cm homogeneous experiment matrix.

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Soil Types*</th>
<th>Amendment</th>
<th>Ion Movement</th>
<th>Duplicate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Low</td>
<td>Lactate</td>
<td>EK</td>
<td>A</td>
</tr>
<tr>
<td>2</td>
<td>High</td>
<td>Lactate</td>
<td>EK</td>
<td>A</td>
</tr>
<tr>
<td>3</td>
<td>Low</td>
<td>Lactate</td>
<td>EK</td>
<td>B</td>
</tr>
<tr>
<td>4</td>
<td>High</td>
<td>Lactate</td>
<td>EK</td>
<td>B</td>
</tr>
<tr>
<td>5</td>
<td>Low</td>
<td>Citrate</td>
<td>EK</td>
<td>A</td>
</tr>
<tr>
<td>6</td>
<td>High</td>
<td>Citrate</td>
<td>EK</td>
<td>A</td>
</tr>
<tr>
<td>7</td>
<td>Low</td>
<td>Citrate</td>
<td>EK</td>
<td>B</td>
</tr>
<tr>
<td>8</td>
<td>High</td>
<td>Citrate</td>
<td>EK</td>
<td>B</td>
</tr>
<tr>
<td>9</td>
<td>Low</td>
<td>Permanganate</td>
<td>EK</td>
<td>A</td>
</tr>
<tr>
<td>10</td>
<td>High</td>
<td>Permanganate</td>
<td>EK</td>
<td>A</td>
</tr>
<tr>
<td>11</td>
<td>Low</td>
<td>Permanganate</td>
<td>EK</td>
<td>B</td>
</tr>
<tr>
<td>12</td>
<td>High</td>
<td>Permanganate</td>
<td>EK</td>
<td>B</td>
</tr>
<tr>
<td>13</td>
<td>Low</td>
<td>Citrate</td>
<td>HC</td>
<td>A</td>
</tr>
<tr>
<td>14</td>
<td>High</td>
<td>Lactate</td>
<td>HC</td>
<td>A</td>
</tr>
<tr>
<td>15</td>
<td>Low</td>
<td>Citrate</td>
<td>HC</td>
<td>A</td>
</tr>
<tr>
<td>16</td>
<td>High</td>
<td>Lactate</td>
<td>HC</td>
<td>B</td>
</tr>
<tr>
<td>17</td>
<td>Low</td>
<td>Bromide</td>
<td>EK</td>
<td>A</td>
</tr>
<tr>
<td>18</td>
<td>Low</td>
<td>Bromide</td>
<td>EK</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Total 18</td>
<td></td>
</tr>
</tbody>
</table>

*HC – hydraulic conductivity

* Soil Types: High = High Hydraulic Conductivity and Low = Low Hydraulic Conductivity

Hydraulic Transport

Two hydraulic transport tests were conducted with sand and citrate. The soil was packed in the cells in the same manner as with the EK experiments. These test were conducted horizontally as were the EK experiments. The hydraulic amendment tank was filled with water with a citrate concentration of 10,000 mg/L and was attached to a constant head bottle with the same concentration of citrate (Figure 8).

A hydraulic unit gradient test (1-cm/1-cm) of was conducted with the amendments. A unit head was applied to the system to push the amendment into the soil. Since the hydraulic conductivity in the sand was high, samples were taken only at the end of the 40-cm length. A large disperse front was observed at the beginning of the concentration front. To eliminate the disperse effect, a second test was conducted with one half unit gradient (1-cm/2-cm) and the cell was operated in an upflow configuration instead of the horizontal configuration (Figure 8). An advective-disperse model was used to fit the data collected. Table 3 lists the results from the model. Figure 9 a and Figure 9 b shows the vertical and horizontal data with the model fit, respectively.

Since the hydraulic transport of the amendment in the clay was slow, pore water samples were removed from the amendment chamber and ports in the side of the soil chamber and analyzed for concentrations of citrate. No citrate or acetate was found from the extracted pore water for over the two month testing period. Degradation of the citrate concentration occurred within the tank. The pH of the tank water remained between, 7.0 and 7.9. The ORP readings were approximately -190 mV.
Table 3: Hydraulic Citrate Transport in Sand

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Horizontal</th>
<th>Vertical</th>
</tr>
</thead>
<tbody>
<tr>
<td>q (cm/hr)</td>
<td>1800</td>
<td>708</td>
</tr>
<tr>
<td>L (cm)</td>
<td>38.74</td>
<td>38.74</td>
</tr>
<tr>
<td>$C_0$ (ppm)</td>
<td>230</td>
<td>88</td>
</tr>
<tr>
<td>A (cm$^2$)</td>
<td>77.42</td>
<td>77.42</td>
</tr>
<tr>
<td>$C_i$ (ppm)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>v (cm/hr)</td>
<td>59.62</td>
<td>24.80</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.60</td>
<td>0.11</td>
</tr>
<tr>
<td>n</td>
<td>0.39</td>
<td>0.37</td>
</tr>
<tr>
<td>error</td>
<td>31265.74</td>
<td>265.54</td>
</tr>
</tbody>
</table>

Figure 8: Photo of hydraulic transport experimental, horizontal and vertical

Figure 9: Hydraulic Transport of Citrate in Sand (a) vertical (b) horizontal
At testing conditions, the measured hydraulic conductivity of sand and clay were $3.5 \times 10^{-3}$ cm/s (302 cm/day) and $2 \times 10^{-7}$ cm/s (0.017 cm/day), respectively. While breakthrough of the amendment in the 40 cm sand sample will occur in less than 3 hours, it is estimated that breakthrough in the clay sample would require 6.5 years to achieve. In fact, it is estimated that more than one year would be required to detect the additive at the first port in the cell (7.5 cm) under a unit hydraulic gradient if the amendment was non-reactive. Two hydraulic transport tests were conducted with the clay soil, one with lactate and one with citrate. Since these experiments were conducted without sterile control, the amendment concentration in the chamber next to the soil biodegraded and the concentration had to be maintained weekly. The pore water was analyzed weekly for the presence of amendments. After more than two months of testing under hydraulic gradient, no amendments were detected in any port pore water samples.

Several duplicate tests were conducted. A summary of the tests that were conducted on clay is displayed. Note that several other tests were conducted on sand and sand/clay samples (which are not listed in this table).

Lactate Transport in Clay:

Two duplicate (4 total) experiments were conducted to evaluate rates of transport of lactate in low permeability clay for a homogeneous, low permeability soil system. Transport rates and profiles of lactate in clay varied depending upon electric current, anolyte/catholyte concentrations, and chemistry. The best results were achieved in the case where the lactate was added to both cathode and anode under 2 A/m$^2$ current density (produced an effective voltage gradient of 1 to 0.5 V/cm) and a high concentration of 10,000 mg/l. Figure 10 shows the increase in lactate concentration in ports 2 and 3 in the clay sample under a current density of 2 A/m$^2$. The results show that lactate appeared after 100 hours of testing and achieved 500-mg/l concentrations in less than 400 hours.
Figure 10: Lactate concentration in ports 2 and 3 (mid section) clay

Figure 11: Lactate Additive Transport in Clay
Measurement of additive transport in clay showed that a relatively uniform lactate concentration of 300 mg/L was achieved after 281 hours of testing and increased to about 800 mg/L after 520 hours (618 hours in the duplicate) of testing. The effective voltage gradient during this period was 0.5 V/cm, which indicates that we can achieve an average transport rate of 3.7 cm/day (3.1 cm/day in the duplicate) under a unit voltage gradient of 1 V/cm. This rate is more than 200 (182 in duplicate) times faster than under a unit hydraulic gradient. Measurement of electroosmosis showed that the coefficient of electroosmotic permeability averaged between 2 x 10^{-5} to 5 x 10^{-5} cm²/Vs, or electroosmotic transport rate of 3 cm/day (under 1 V/cm gradient). Although this is a significant transport rate from anode to cathode, the results show that ion migration rate from cathode to anode is much more significant such that it produced a net transport rate of 3.7 cm/day (under 1 V/cm). This indicates that the total ion migration rate in the soil is 6.7 cm/day. Further control of electroosmosis can enhance the process and may double the transport rate.

Figure 10 and clearly show that although lactate concentration in the soil did not reach boundary values of 10,000 mg/L, the process was effective in transporting significant concentrations of lactate into a low permeability soil ($k_h = 0.0017$ cm/day).

Citrate Transport in Clay

Two experiments were conducted to evaluate rates of transport of citrate in low permeability clay. Transport rates and profiles of citrate in clay varied depending upon electric current, anolyte/catholyte concentrations, and chemistry. The best results were achieved in the test where the citrate was added to both cathode and anode under 5.2 A/m² current density (produced an effective voltage gradient of 1.25 to 0.75 V/cm) and a high amendment concentration of 10,000 ppm. At the end of the experiment, the soil was removed from the cell in five vertical sections. Some of the soil was centrifuged at 10,000 rpm for 30 minutes. The supernate was extracted from the centrifuge tubes and analyzed by ion chromatography. Figure 12a and Figure 12b, shows the experiment with the highest concentrations of acetate and citrate the end of the test. These results illustrate that high concentrations of citrate and acetate can be delivered to low permeable soils using EK. After completing 546 hours of testing, acetate concentrations in the pore water ranged from 1,400 to over 2,500 mg/L across the cell. Citrate concentrations ranged from 5 to 18 mg/L.
The pH and oxidation-reduction potential (ORP) values are listed in Table 4. These values show that when the pH of the electrode chambers are controlled that the pH and ORP values remain relatively constant. The ORP measurements remain high as long as an electric potential is applied. After power is turned off, microbes in the soil will begin to consume the amendments and the ORP will begin to drop reducing conditions.

<table>
<thead>
<tr>
<th>Distance from Anode (cm)</th>
<th>8</th>
<th>16</th>
<th>24</th>
<th>32</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citrate Soil A pH</td>
<td>8.3</td>
<td>8.2</td>
<td>8.2</td>
<td>8.1</td>
<td>7.9</td>
</tr>
<tr>
<td>Citrate Soil A ORP</td>
<td>92.5</td>
<td>91.0</td>
<td>106.0</td>
<td>114.5</td>
<td>130.5</td>
</tr>
<tr>
<td>Citrate Soil B pH</td>
<td>8.4</td>
<td>8.3</td>
<td>8.3</td>
<td>8.3</td>
<td>8.0</td>
</tr>
<tr>
<td>Citrate Soil B ORP</td>
<td>89.5</td>
<td>120.5</td>
<td>110.5</td>
<td>111.5</td>
<td>120.0</td>
</tr>
</tbody>
</table>

Non-Reactive EK Transport in Clay
Two tests were conducted using bromide under a current density of 5.3 A/m² and were processed for 288 hours. Bromide concentration of 1000 mg/l was used at the cathodes. In one of the tests, there were some difficulties in extracting the sample.
for chemical analysis. However, these problems were properly addressed in the second test. The results showed that bromide migrates through the 40-cm cell in less than 100 hours. Figure 13 shows the bromide concentration after 72 hours of testing. It is clear that bromide has reached the last port close to the anode. These concentrations indicate a transport rate greater than 13 cm/day. This is much faster than the rate of transport of lactate and citrate, mainly because of the significant biodegradability of the organic acid anions. The results prove that transport under dc field is a significant transport mechanism, considering the very low soil permeability.

![Bromide non-reactive EK test](image)

Figure 13: Bromide non-reactive EK test

Permanganate in Clay 40cm cells

Two experiments with the permanganate in clay ran with a voltage gradient of 0.8 V/cm and a current density of 1.2 A/m². After 500 hours of operation, permanganate failed to migrate into the soil. A thin wall of manganese oxide (noted by the brown color) was discovered at the cathode chamber interface. It is believed that the iron content in the clay exerted demand for the permanganate beyond the 10,000 ppm concentration maintained.

Lactate Transport in Sand

Transport of lactate in sand was efficient and occurred at a rate of 5 cm/day under a unit voltage gradient of 1 V/cm. Figure 14 shows concentration profile of lactate in sampling ports during processing. The figure shows that lactate reached ports 4 and 3 (about half of the sample length in less than 100 hours. The figure shows that an increase occurred in anolyte concentration but at a slow rate. Oxidation at the anode is expected to impact the stability of lactate as it moves from the cathode towards the anode. Furthermore, biological transformation of lactate affected the transport and limited the increase in lactate concentration across the soil. A maximum concentration of 6,000 mg/l was achieved in the sand. It was surprising that significant electroosmotic
flow occurred in the sand experiments, such that the coefficient of electroosmotic permeability was about $2 \times 10^{-5}$ cm$^2$/Vs. Under a unit voltage gradient (1 V/cm), this electroosmosis produced a reversed transport rate of 1.7 cm/day. It was interesting that the net lactate transport was significant from the cathode towards the anode at a rate of 5 cm/day, which means that the ion migration component of transport was high (more than 6.7 cm/day) such that the net flow (ion migration minus electroosmosis is 5 cm/day).

![Figure 14: Changes in lactate concentration in sand](image-url)
It is critical to evaluate the pH changes during the experiment, since it will significantly impact microbial activity. Electrolysis pH changes will be more significant in sand (than clay) because transport is faster in sand and it has a very low buffer capacity. However, our goal is to maintain neutral pH conditions. Figure 15 shows final pH distribution in the sand experiment (2 A/m² current density after 381 of processing). Testing under controlled conditions demonstrated neutral conditions in the soil could easily be maintained and the impact of electrolysis on soil pH is minimal. In clay, the problem is less critical since the transport process is slower and clay has a significant buffer capacity.

In any case, transport rate by ionic migration is significantly less than transport under unit hydraulic gradient for this sand (The hydraulic conductivity of the sand is about 300 cm/day). However, while the ratio of transport in sand to transport in clay is 17500 under hydraulic gradient, the ratio is less than 2 under dc field. This clearly demonstrates that the relatively uniform transport that can be achieved in heterogeneous soils under dc field will never be possible under a hydraulic gradient.

Citrate Transport in Sand

Two duplicate experiments (4 test) were conducted to determine the transport rate of citrate in the highly permeable sand. Transport of citrate in sand occurred at a rate of 26 cm/day under a unit voltage gradient of 2.6 V/cm and at 20 cm/day at voltage gradient of 1 V/cm. Figure 16 shows concentration profile of citrate in sampling ports during processing. The figure shows that citrate reached ports 2 and 1 (about half of the sample length in less than 40 hours. The figure shows that an increase occurred in anolyte concentration but at a slow rate. Oxidation at the anode is expected to impact the stability of lactate as it moves from the cathode towards the anode. Because of the
short duration of these test little transformation of citrate occurred across the soil. A maximum concentration of 3,000 mg/l was achieved in the sand.

Figure 16: Citrate Concentration Changes Transport through Sand

Permanganate in sand in 40cm cells

Two experiments with the permanganate in sand ran with a voltage gradient of 0.8 V/cm and a current density of 1.2 A/m². Permanganate was maintained at a concentration of 5,000 mg/L as MnO4 in the cathode compartment. The permanganate moved through the sand at a rate of 7.9 cm/day. After 122 hours of operation, permanganate reached the anode compartment. Figure 17 shows the migration of permanganate through the EK cell.

Figure 17: Photos of Permanganate EK Transport through Sand
Heterogeneous EK amendment tests
Tests were performed to evaluate efficiency of additive transport in heterogeneous soil under dc fields. The tests consisted of placing the soil in layers into the cell to represent soil heterogeneity (Figure 5 and Figure 6b). For this task, duplicate experiments were conducted using the amendments: lactate, citrate and permanganate. In the heterogeneous experiments, the soil was packed in three layers of equal depth. The upper and bottom layers are sand, while the middle layer consists of a clay layer in sand arrangement as shown in Figure 5. Table 5 lists the heterogeneous experiments.

Table 5: Layered Soils 40 cm Cells Experiments

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Amendment</th>
<th>Ion Movement</th>
<th>Duplicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lactate</td>
<td>EK</td>
<td>A</td>
</tr>
<tr>
<td>2</td>
<td>Citrate</td>
<td>EK</td>
<td>A</td>
</tr>
<tr>
<td>3</td>
<td>Permanganate</td>
<td>EK</td>
<td>A</td>
</tr>
<tr>
<td>4</td>
<td>Lactate</td>
<td>EK</td>
<td>B</td>
</tr>
<tr>
<td>5</td>
<td>Citrate</td>
<td>EK</td>
<td>B</td>
</tr>
<tr>
<td>6</td>
<td>Permanganate</td>
<td>EK</td>
<td>B</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>6</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Lactate Transport in 2D
Transport in the heterogeneous samples showed interesting results. Concentration of lactate increased in the upper sand layer within the first 100 hours to few thousands mg/l (Figure 18). After 100 hours testing, the concentration of lactate showed an increase but at a slower rate. This was probably the result of transformation of lactate due to biological activity and chemical redox at the anode. Similar to the experiments using sand only, the maximum concentration achieved in sand is 6000 mg/l in port 4, while ports 3 and 2 reached concentrations of 4000 and 3000 respectively. The concentration at port 1 fluctuated between 2000 and 300 mg/l. The concentration continued decreasing towards the anode, where it was 1350 mg/l.
Figure 18: Lactate Concentration in ports 2 and 4 (in upper layer – Sand)

Figure 19: Lactate Concentration in Clay (ports 2 and 3 - Clay)
In the middle clay layer, it took 200 hours for lactate to show up in the sampling ports (Figure 19), and the increase was more significant in port 3 (cathode side). The concentration increased to more than 700 mg/l in port 3 and to 600 mg/l in port 2. Transport rates calculated are equivalent to those calculated from the clay only experiments. The results again demonstrate the significance of ion migration as compared to electroosmosis.

An interesting result was the increase in water content in the clay layer, which also occurred in the clay only experiments (Figure 20). This change could be due to physicochemical effect on the clay mineralogy and microstructure. However, since there was no change in the pH, it is also believed that the process causes swelling due to development of a positive pressure in the soil because of the non-uniform electroosmosis profile. Further tests are needed to verify this behavior.

Citrate Transport in Heterogeneous Soil System

Two experiments were conducted to evaluate feasibility of transporting citrate into a clay layer surrounded by sand. Does the amendment follow the electrical field lines through the low permeability soil areas or will the amendment bypass the clay through the highly permeable sand as is observed with hydraulic amendment delivery. The best results were achieved in the test where the citrate was added to cathode only under 5.2 A/m2 current density (produced an effective voltage gradient of 1.25 to 0.75 V/cm) and a high concentration of 10,000 mg/l. At the end of the experiment, the clay was removed from the cell in five top and five bottom sections. A portion of the soil was centrifuged at for 30 minutes. The supernate was extracted from the soil by centrifuge and analyzed by ion chromatography. Figure 21a and Figure 21b, shows the experiment with the highest concentrations of acetate and citrate the end of the test. These results illustrate that high concentrations of citrate and acetate can be amended.
to low permeable clays by EK even if isolated by a high permeable layer. After completing 452 hours of testing, acetate concentrations in the pore water ranged from 2,400 to over 3,300 mg/L across the cell. Citrate concentrations ranged from 55 to 223 mg/L.

Figure 21: Heterogeneous citrate test, final pore water analysis

Permanganate in Heterogeneous 40cm cells

Two experiments with the permanganate in clay ran with a voltage gradient of 0.8 V/cm and a current density of 1.2 A/m². Initially 5,000 mg/L as MnO₄⁻ was maintained in the cathode compartment. The permanganate migration moved quickly into the soil from the cathode chamber. After approximately 96 hours of operation, the purple permanganate color at the leading edges changed to a brown color. This color change indicates that oxidation of permanganate to manganese oxide has occurred. In fact, the permanganate migration stalled completely. This condition was allowed to persist for approximately 240 hours. After this, the permanganate concentration in the cathode chamber was increased from 5,000 to 10,000 mg/L as MnO₄⁻. Approximately 48 hours after increasing the concentration, the permanganate demand areas were overcome with the higher permanganate concentration. Figure 22 a, b, and c illustrates the sequence of these events. Never the less, as with the homogeneous clay EK experiment, the permanganate failed to penetrate clay soil.
Homogeneous 1 and 2 meter EK Experiments.
Permanganate in 2-meter high permeable soil

The rate of migration for the potassium permanganate test was measured visually. A measuring tape was used to monitor the leading edge of the permanganate front from the cathode chamber each day (Figure 23). The migration rate of permanganate was calculated to be 27.3 cm/day (Figure 24). Just before the permanganate front reached the anode chamber, samples across the length of the EK cell were taken (Figure 25). The Voltage gradient was 1.47 V/cm and the current density was 1.53 A/m².
Experiments were conducted to evaluate rates of transport of citrate in sand in over a longer distance. The results were achieved by adding citrate to the cathode under a current density of 1.8 A/m² (produced an effective voltage gradient of 2.2 to 5.5 V/cm) and a high concentration of 10,000 mg/l. After completing 118 hours of testing, acetate concentrations began to appear in the anode compartment. After 192 hours of
testing, citrate was detected in the anolyte. Citrate concentrations ranged from 493 to 667mg/L throughout the sand. A sample profile of the citrate concentration was taken from ports across the cell before termination of the test. The citrate concentration as well as pH, ORP are show in Table 6. The citrate migration rate was calculated to be 12.5 cm/day. The migration rate of the citrate may have been retarded by the high concentration of nitrate in the system when the citrate was introduced. The citrate ion may lose its charge as it migrates though the cell. Biological degradation of the citrate could also be a factor. Evidence of this is supported by the presence of acetate in the system.

Table 6: Citrate Concentration across 1-meter cell

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Distance for Anode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>c<strong>i</strong>trate</td>
<td>29.3</td>
</tr>
<tr>
<td>acetate</td>
<td>6.9</td>
</tr>
<tr>
<td>pH</td>
<td>7.34</td>
</tr>
<tr>
<td>ORP</td>
<td>203</td>
</tr>
</tbody>
</table>

Citrate in 2-meter Sand

A 2-meter EK experiment in sand with citrate as the cathode amendment was conducted. Because the long cell had a small cross sectional area, it was difficult to achieve electrical equilibrium before introducing the citrate amendment at the cathode. To shorten the equilibration time, the cell was initially set up with 500 ppm of sodium chloride. The brought the system to a stable current density of 1.48 A/m². The initial breakthrough rate of citrate electromigration from anode to cathode for the 2-meter sand with citrate was approximately 28 cm/day. The migration rate is the same as the permanganate.

Citrate in 1-meter Clay

The 1-meter clay with citrate amendment experiment ran for 59 days. A citrate amendment was added to the cathode for 59 days while the citrate amendment was added to the anode for 52 days. Samples were taken from the soil periodically to assess the citrate ion movement. The pore sample analysis revealed acetate ions were present in the soil pore water. Upon termination of the experiment, pore fluid was extracted from the soil in sections by centrifuge. The analysis revealed that citrate and acetate were present in all soil sections. The degradation of the amendment in the soil during the electrokinetic process makes it difficult to calculate accurate transport rates. The citrate concentrations in the pore water solutions ranged for 2 to 116 mg/L. Acetate concentrations ranged for the same soil sections ranged from 10 to over 2900 mg/L. The apparent electroosmotic flow rate was calculated to be 0.77 cm/day and the apparent ion migration rate was 1.02 cm/day. Figure 26 a and b shows the final pore water citrate and acetate concentrations.
Evaluation of EOP on amendment transport and mixing

The objective of this task was to determine the effect of EOP enhanced EK treatment on amendment transport and dispersion in the soil. These experiments consisted of homogeneous EK experiments performed on the low permeable soil using citrate as the amendment.

Various electrokinetic (EK) experiments were performed at ERDC-CERL (U.S. Army Corps of Engineer’s Engineer Research and Development Center – Construction Engineering Research Laboratory located in Champaign, IL; hereafter CERL) in support of this project. One-dimensional transport tests were conducted. Experimental cells and pH control procedures identical for all participants were used, however, it was decided to use metallic electrodes coated with mixed metal oxides manufactured by CerAnode Technologies in place of the graphite electrodes used at EL. This type of electrode is better suited for the harsh environments found in field-testing situations. The mixed metal oxide coating is a semiconductor that significantly reduces the rate of metal consumption and allows for the use of higher current densities compared to conventional graphite electrodes. In addition, effectively no metal ions will be solubilized and introduced into the test system. The electrodes were fabricated to match the dimensions of the graphite electrodes used at EL.
One-dimensional tests were performed on two separate occasions. A picture of the experimental apparatus in use is shown in Figure 27.

The first experiment was operated for a total of 21 days. A typical Gessie Loam type soil provided by EL was saturated to a moisture level of 24% by weight and compacted into the test apparatus using a standardized procedure. The pH was controlled at the anode by introducing 0.2M sodium hydroxide solution using a pH control system. The pH at the cathode was controlled with a 0.1M citric acid solution using the same apparatus. Sodium citrate was introduced into the cathode chamber at a concentration of 10,000 ppm citrate. Concentrated 60,000 ppm sodium citrate solution was added periodically in an attempt to maintain the citrate concentration in the anode chamber at 10,000 ppm. A time asymmetric, reversing polarity pulsed electric field was applied to the sample for the duration of the experiment. The characteristics of the specific pulse used for this experiment is shown in Figure 28.

![Current Pulse used in Experiment 1](image)

Using this type of imposed electric field has the distinct advantage of slowing the production of acid at the anode. In situations where the pH of the anode well is not controlled, a pulsed electric field will slow the migration of the acid front into the soil matrix thereby maintaining the electro-osmotic effect and reducing the amount of heavy metal ion precipitation within the treatment zone. In this experimental situation, the pH of the anode and cathode wells is controlled, so acid migration is thought not to be a
significant problem, but the pulsed field should decrease the amount of buffer solution needed to maintain a steady pH in the well, which would become a distinct advantage for a larger field scale apparatus. As shown in Figure 28, a current of 20 mA was applied for 10 seconds. After this time period, the current was switched to –5 mA for 3 seconds, and the cycle would continue. Samples were drawn daily from four evenly spaced ports along the length of the soil cell and from the anode and cathode chambers. In addition, the voltage profile was measured across the length of the cell with the same frequency. The profiles at selected time intervals are presented in Figure 29.

Figure 29: Voltage profiles measured during pulsed electric field experiment

It can be seen that the addition of sodium hydroxide at the anode rapidly increases the conductivity of the solution in the anode chamber, thereby lowering the voltage necessary to maintain the set current levels. In addition, between ports 4 and 1, it can be seen that the slope of the voltage profile is approximately constant across the measured time intervals. This slope quantifies the conductivity of the pore solution. A decrease in slope would correspond to an increase in conductivity and vice versa. A change in conductivity would result when more free ions, i.e. sodium ions, migrate into the test section. It is unlikely that sodium ions failed to migrate into the soil matrix, so the more likely explanation for this is that a steady state was reached early in the experiment.

Pore water extraction and analysis is a complex process. Modest funding levels prevented CERL from completing the development of a robust pore water sample collection and analysis procedure, so the chemical analysis data is incomplete. However, some useful and indicative data was collected. Work done at EL has shown that citrate ions tend to degrade into several other species, acetate being the most prolific, when introduced into the soil matrix. This has been independently verified by
CERL. Analysis using HPLC performed at the Waste Management and Research Center at the University of Illinois detected acetate ions in several of the pore water solutions, but failed to detect any citrate ions. Acetate concentrations in pore water samples extracted from port 1 (that nearest cathode) and port 4 (that nearest anode) for the first four days of operation as shown in Table 7. Subsequent data and data for ports 2 and 3 are not available because of inadequate sample volumes or sample preparation.

Table 7: Acetate concentrations in pore water extracted during pulsed experiment

<table>
<thead>
<tr>
<th>Day</th>
<th>Port 1</th>
<th>Port 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 1</td>
<td>N/A</td>
<td>66 ppm</td>
</tr>
<tr>
<td>Day 2</td>
<td>N/A</td>
<td>164 ppm</td>
</tr>
<tr>
<td>Day 3</td>
<td>366 ppm</td>
<td>90 ppm</td>
</tr>
<tr>
<td>Day 4</td>
<td>386 ppm</td>
<td>123 ppm</td>
</tr>
</tbody>
</table>

This data suggests that the citrate ions are migrating into the soil and rapidly converting to acetate ions.

A second one-dimensional experiment was performed using a direct current electric field in place of the pulsed electric field. The same soil was used and moistened until the water content of the soil reached 24%. All other experimental variables were identical to the previous experiment. The test was allowed to continue for 14 days. Voltage profiles were measured, and pore water samples were collected in the same manner as that in the previous experiment. Several voltage profiles taken throughout the course of the experiment are shown in Figure 30.

Figure 30: Voltage profiles measured during dc electric field experiment

As in the previous experiment, the conductivity in the anode chamber increases with time while the conductivity in the pore water seems to remain almost constant although this plot seems to indicate a slight increase in pore water conductivity between
7 and 12 days. The chemical analysis of pore fluid samples for this experiment was performed at EL. Data is available only for the final 7 days of the experiment for pore water from port 1 and solution taken directly from the anode chamber. Once again, the presence of citrate was not detected, while significant amounts of acetate were found. The results are given in Table 8.

Table 8: Acetate concentrations in solution extracted during pulsed experiment

<table>
<thead>
<tr>
<th>Day</th>
<th>Port 1 ppm</th>
<th>Anode Chamber ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 7</td>
<td>575.20</td>
<td>0.22</td>
</tr>
<tr>
<td>Day 8</td>
<td>953.11</td>
<td>0.22</td>
</tr>
<tr>
<td>Day 9</td>
<td>895.96</td>
<td>0.21</td>
</tr>
<tr>
<td>Day 10</td>
<td>1,132.79</td>
<td>0.22</td>
</tr>
<tr>
<td>Day 11</td>
<td>1,112.20</td>
<td>0.30</td>
</tr>
<tr>
<td>Day 12</td>
<td>1,136.90</td>
<td>0.16</td>
</tr>
</tbody>
</table>

The results show an increasing concentration of acetate ions in the pore water closest to the cathode and that these ions have effectively migrated completely through the soil sample into the anode chamber. The demonstrated distance of migration is the full test cell length (40 cm).

CERL also completed some initial work on optimizing a pulse for ion delivery. Due to the need for multiple repeated experiments, a small-scale model of the one-dimensional cell was constructed and used in these experiments. A picture of this apparatus appears in Figure 31.

![Figure 31: Picture of small-scale one-dimensional apparatus](image)

The duration of the tests were also significantly shortened to 36 hours. A kaolinite type clay was mixed with a 100 mg sodium chloride per 250 mL deionized water solution to a water content of approximately 30%. This clay mixture was compacted into the test cell, and the anode chamber was filled with the aforementioned
saltwater solution. An equal volume of 6,000 ppm sodium citrate solution was placed in the cathode chamber. Three identical experiments were performed changing only the characteristics of the electric field pulse. Diagrams of the pulses used in each experiment are shown in Figure 6 below.

Figure 32: Voltage profiles used in optimization experiments

Upon completion of each of the tests, samples were taken from each of the anode and cathode chambers. These samples were analyzed at CERL using an ultraviolet spectroscopy method. The results are shown in Figure 33 and Figure 34. The height of the peak of the wave indicates the relative concentrations of the samples. The wavelength corresponding to the peak indicates the chemical species present as each ion reflects the ultraviolet radiation at a unique wavelength. It should be noted that no data is available from the cathode of the experiment using pulse 3.

Figure 33: Cathode UV Data
The initial data suggests that pulse optimization could yield improved migration of amendment (e.g. mass flow per unit power requirements) into a contaminated zone. The amount of citrate in the cathode chamber serves as an inverse indicator of the amount migrated toward the anode. For two sets of pulse characteristics (pulse 1 and pulse 2, see [Figure 33] there is a comparative increase in the amount migrated toward the anode for otherwise comparable conditions. This occurs even though the duty cycle factor (net voltage magnitude weighted time average in the forward direction toward the anode) is less. The net power per unit time is also less. Also, the wavelength corresponding to the peak of the graph representing the ion present in the anode chamber is significantly different from that of the citrate ion that was introduced into the cathode chamber. This seems to suggest that the citrate is degrading into a different ionic species, as was the case for the larger scale one-dimensional experiments conducted previously. Owing to project constraints, a calibration curve was not constructed to quantify the absolute concentrations of the samples. More work is needed in this area to improve the analysis technique and to perform more experiments in search of an optimized waveform.

Figure 34: Anode UV Data
Cost Components

The total costs for full-scale in situ implementation of the proposed EK enhanced bioremediation process can be divided into five major components: (1) costs for fabrication and installation of electrodes, (2) cost of electric energy, (3) cost of enhancement agents, (4) costs of any post-treatment, if necessary, and (5) fixed costs. Electrode configuration and spacing impact these cost components as described below.

Electrode cost depends upon the number of electrodes per unit surface area and is given by,

\[ C_{\text{electrode}} = C_1 N \]

where \( C_{\text{electrode}} \) ($/L^3) is electrode costs per unit soil volume, \( N \) (L^{-2}) is the number of electrodes per unit surface area, which is dependant upon configuration and spacing, and \( C_1 \) ($/L^{-1}) is the cost of electrodes per unit length. Increasing electrode spacing decreases the value of \( N \) and hence decreases total electrode costs. Spacing between electrodes of same polarities significantly impacts this cost component.

Several factors affect energy requirements and cost for enhanced EK bioremediation at a specific site. These factors include soil and groundwater properties, contaminant properties, electrode configuration and processing time. Energy consumption changes during processing due to changes in electric conductivity. However, energy calculations could by simplified by averaging soil electrical conductivity throughout the process. Accordingly, energy expenditure per unit volume of contaminated soil is given by the following equation

\[ W = \phi_{\text{max}} I T_R L \]

where: \( W \) (J/L^3) is energy expenditure per unit volume of soil and \( \phi_{\text{max}} \) (V) is the total applied voltage, \( I \) is the current density (Amp m^{-2}), \( T_R \) is the time required for remediation and \( L \) is the anode/cathode spacing. \( C_{\text{energy}} = C_2 W \)

where \( C_{\text{energy}} \) ($/L^3) is electric energy cost per unit volume of soil treated, and \( C_2 \) ($/kWh) is electric energy cost.

Enhancement agents and chemicals are injected to stimulate conditions for anaerobic transformation. Chemicals include organic acids such as lactic and citric acids. Chemical cost is a significant component of the total cost of the processes. Chemical cost is dependent upon the electric current and can be estimated by the following equation, 

\[ C_{\text{chemical}} = \frac{C_3 I}{L} \frac{M_w}{\alpha F} T_R \]
where $C_{\text{chemical}}$ ($\text{L}^{-3}$) is the cost of chemicals required per soil volume, $C_3$ ($\text{M}^{-1}$) is the cost of the chemical agent, $M_W$ ($\text{MM}^{-1}$) is the molecular weight of the chemical, $\alpha$ (dimensionless) is a factor depending upon the stoichiometry of the neutralizing reaction, and $F$ is Faraday’s constant (96,485 C/mol-electron). Chemical cost is dependent on soil and contaminant characteristics. Post treatment costs should also be considered if effluent treatment is required. However, since the objective is to degrade the contaminant in-situ, it is expected that the effluent post treatment cost will not be significant.

Other costs for full-scale implementation include mobilization and demobilization costs of various equipment, site preparation, security, progress monitoring, insurance, labor, contingency, and miscellaneous expenses. The equipment will not be consumed in a particular project. However, there are capital, depreciation, or rental costs involved. These cost components will be divided into fixed (e.g. mobilization and demobilization) and variable (e.g. monitoring, insurance, rentals) components. Variable costs are simply evaluated by multiplying the cost rate by the total time required for remediation.

**Example Cost Evaluations**

The following example is considered to show the role of each cost component. In this example, a contaminated area of 30 m x 60 m is assumed. The depth of contamination is assumed to be 3 m. The soil is saturated clay. The porosity, tortuosity factor, electrical conductivity, and coefficient of electroosmotic permeability of the soil are determined from preliminary laboratory analyses to be 0.4, 0.3, 0.02 S/m, and 2x10^{-9} m^2/V-s, respectively. The ionic mobility of organic additives is taken to be 5x10^{-8} m^2/V-s. A delay factor of 4 can be assumed to account for the transformation rates after delivering the additives to the contaminated sites (i.e. multiply the time required for delivery by a factor of 4 to calculate the total time required for remediation).

The mobilization cost of a drilling rig and the labor cost of a two-man operating crew are taken to be $1000 per day to evaluate $C_1$. For boreholes to be drilled without installation of casing and sampling, a continuous flight auger can achieve approximately 65 m a day. Therefore, the drilling cost is estimated to be $15 per linear meter. Costs for fabrication and installation of electrodes are approximately $5 per linear meter as the electrodes are reusable. Therefore, $C_1$ is taken to $20 per linear meter. The electricity cost $C_2$ is assumed $0.04 per kWh. Cost of enhancement organic chemical (molecular weight assumed 100 g/mole) is taken as $2 / kg. Variable cost rate is calculated based on two-man crew, 14 hours per week, at a rate of 25 $/ man-hr. Accordingly, the variable rate will be around 0.001 $/m^3-hr, including 30% increase for insurance. Total cost of other components, including post treatment and fixed costs, is taken as $25 / m^3.

Consider electrode configuration where the same-polarity electrode spacing equals one-third the anode-cathode spacing. Impact of electrode spacing on electrode, energy, and variable costs is demonstrated in cost Figure 1 below. In this figure, an electric gradient of 100 V/m is assumed for cost evaluations. Increasing electrode spacing showed a significant decrease in electrode costs. Increasing electrode spacing from 1 m to 2 m resulted in a more than 80% decrease (from $60 /m^3 to about $10 /m^3) in electrode costs. However, increasing electrode spacing beyond 2 m did not result in a comparable decrease in electrodes cost.

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Wider electrode spacing results in linear increases in energy and variable costs. As indicated earlier, wider electrode spacing will increase the total voltage applied (assuming constant voltage gradient), increase energy expenditure and cost. Similarly, wider electrode spacing increases time requirements and, consequently, variable costs. Impact of electrode spacing on total costs and time requirements is displayed in Figures 2. A minimum cost exists between the cost and the electrode spacing relationship. It is necessary to provide a mechanism for selecting the optimum electrode spacing that will minimize cost, time, or both.

Under these practical assumptions, it is clear the process design significantly impacts the time and cost of remediation. Under the conditions provided in this analysis, the cost of remediation can be on the order of $100 per cubic meter. Of course, other practical condition and site complications may cause an increase in this cost and may reach $200 per cubic meter.
Figure 1

Impact of electrode spacing on electrode, energy and variable costs for 1-D application (refer to text for parameter values).
Figure 2

Time requirements and costs as a function of electrode spacing for 1-D applications (refer to text for parameter values).
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